Stable Carbocations. Part 18.[1] Hydride-transfer Reactions of [(η5-Cyclohexadienyl)(η5-cyclopentadienyl)iron]alkylium Ions

By **Mohammed M. Khan** and **William E. Watts**,* School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland

In solution in CF_3CO_2H, (η5-cyclohexadienyl)(η5-cyclopentadienyl)iron derivatives containing a $C(OH)R^1R^2$ substituent attached either to the cyclopentadienyl ring or to C(1) of the cyclohexadienyl ring are converted into (η6-arene)(η5-cyclopentadienyl)iron cations by hydroxy loss and hydride transfer. The mechanism of the reaction has been investigated using deuterium-labelled substrates.

STABILISATION of a carbocation by incorporation of an organotransition metal residue is a well documented phenomenon.[2] The effect has been most thoroughly studied for the iron-group metallocenes[3] but other systems function in a similar although usually less effective manner, e.g. tricarbonyl(η4-butadiene)iron,[4] tricarbonyl(η4-cyclobutadiene)iron,[5] (η4-cyclobutadiene)-(η5-cyclopentadienyl)cobalt,[6] cymantrene and related phosphine complexes,[7] benchrotrene,[8] and nonacarbonyl-(methinyl)tricobalt.[9] We now report an investigation of the ability of the (η5-cyclohexadienyl)(η5-cyclopentadienyl)iron system to stabilise an attached carbocationic substituent.[10]
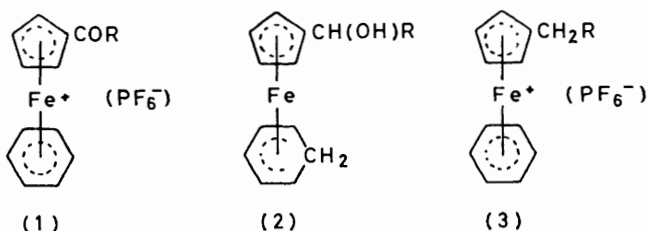
Synthetic Methods.—By analogy with the chemistry of ferrocenylcarbocations,[3] generation of the title cations by acid-promoted dehydroxylation of derivatives containing a $C(OH)R^1R^2$ ring substituent was envisaged. The synthesis of alcohols of this type was accomplished as follows.

The ketonic salts (1a and b) were prepared as previously described[11] from acetyl- and benzoyl-ferrocene, respectively, by cyclopentadienyl ligand exchange with benzene in the presence of Al_2Cl_6. These reactions also afforded[11] minor amounts of the parent complex (4a) but separation of this impurity proved unnecessary (see later). On treatment with an excess of $NaBH_4$ in 1,2-dimethoxyethane, the salts (1a and b) underwent addition of hydride both at the carbonyl group and at the benzene ligand. The corresponding secondary alcohols (2a and b) were isolated following hydrolysis of the reaction mixtures and purified by chromatography (neutral Al_2O_3) which allowed easy separation of the non-polar by-product (5a) resulting from hydride reduction of the contaminant (4a) present in the starting materials.
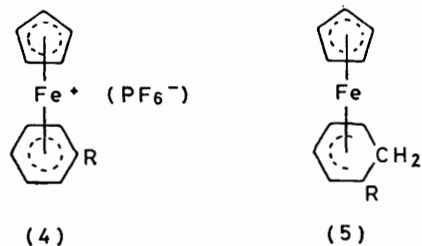
Derivatives containing a hydroxyalkyl substituent at C(1) of the cyclohexadienyl ligand were obtained from the ester (5b), whose preparation by borohydride reduction of the complexed methyl benzoate salt (4b) has been reported[12] earlier. Treatment of the ester (5b) in ether with $LiAlH_4$ and with MeLi, followed by hydrolysis, gave the corresponding primary (5c) and tertiary (5d) alcohols. In the former reaction, careful control of the conditions was necessary (see Experimental section) to avoid further reduction to the 1-methylcyclohexadienyl derivative (5e). This complex has previously been

synthesised, in a mixture with its 2- and 3- methyl isomers, by borohydride reduction of the complexed toluene salt (4c).[13]

In connection with the mechanistic study described
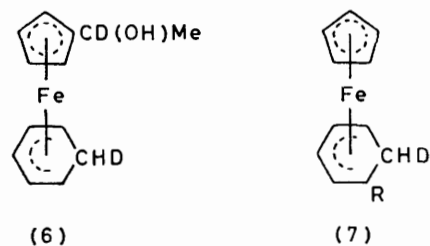

a; R = Me
b; R = Ph

(1)   (2)   (3)

a; R = H
b; R = CO_2Me
c; R = Me
d; R = $CHMe_2$
e; R = $CDMe_2$

a; R = H
b; R = CO_2Me
c; R = CH_2OH
d; R = CMe_2OH
e; R = Me

(4)   (5)

a; R = CO_2Me
b; R = CMe_2OH

(6)   (7)

later, unambiguous synthesis of several reference compounds was also necessary. The ethyl- and benzyl-cyclopentadienyl complexes (3a and b) were prepared by conventional [14] Al_2Cl_6-catalysed ligand-exchange reactions of 1,1'-diethyl- and 1,1'-dibenzyl-ferrocene with benzene. The toluene and cumene analogues (4c and d) were likewise obtained from ferrocene by ligand exchanges with the arenes. The doubly deuterium-labelled alcohol (6) was prepared by reduction of the salt (1a) with $NaBD_4$ in 1,2-dimethoxyethane [cf. preparation of (2a)]. Reduction of the salt (4b) with $NaBD_4$ afforded the deuterium-labelled ester (7a) which was converted into the tertiary alcohol (7b) by reaction with MeLi followed by hydrolysis [cf. preparation of (5d)]. In these labelled substrates (6) and (7a and b), the deuterium

Since the CR_2OH groups (R = H and Me) of the alcohols (5c and d) and (7b) are attached to a dissymmetric residue, the R groups in each molecule are diastereotopic and show well resolved chemical shift distinction. The differences (signal absences and inter-proton coupling patterns) observed between the spectra of the deuterium-labelled complexes (6), (7a and b), (9), and (11) and of their all-proton analogues (2a), (3a), and (5b and d) were entirely consistent with the label sites indicated; in particular, the spectra of the alcohols (6) and (7b) and the ester (7a) lacked the characteristic [15] high-field cyclohexadienyl 6-exo-proton signal present in the spectra of their unlabelled relatives.

Hydride-transfer Reactions.—By analogy with the behaviour [3] of (1-hydroxyalkyl)ferrocenes, which afford

SCHEME 1   Reagents: i, $LiAlH_4$–Et_2O; ii, $LiAlD_4$–Al_2Cl_6– Et_2O; iii, PhH–Al_2Cl_6–Al, then H_2O, then NH_4PF_6

atom attached to the cyclohexadienyl ligand can be confidently assigned the 6-exo configuration since exclusive exo-addition of nucleophiles, including hydride (deuteride), to cationic arenemetal complexes is well established.[15,16] Analogues of the salt (3a) selectively labelled at the α-carbon of the ethyl group with one and with two deuterium atoms [i.e. (9) and (11), respectively] were obtained from 1,1'-diacetylferrocene by the routes indicated in Scheme 1.

The alcohols (2a and b), (5c and d), (6), and (7b) were quite unstable both in solution and in the absence of solvent, and satisfactory elemental analyses were not obtained. However, the i.r., [1]H n.m.r., and mass spectroscopic properties (see Experimental section) of these and the other compounds prepared were fully consistent with the assigned structures. The i.r. spectra (CCl_4 solutions) of the alcohols each contained an intramolecularly Fe-bonded hydroxy stretching absorption at ca. 3 500 cm^{-1}, as found [17] also for the structurally similar (1-hydroxyalkyl)ferrocenes. The [1]H n.m.r. spectra (Tables 1 and 2) were particularly characteristic.

stable ferrocenylcarbocations in acidic solutions, it was anticipated that dissolution of the alcohols (2a and b) and (5c and d) in CF_3CO_2H would lead to the generation of the carbocations (12a and b) and (13a and b), respect-

a; R = Me   a; R = H
b; R = Ph   b; R = Me

ively. However, the [1]H n.m.r. spectra of these solutions showed that rearrangement had occurred in each case to give (η^6-arene)(η^5-cyclopentadienyl)iron cations; i.e. (2a and b) and (5c and d) were converted into (3a and b)

and (4c and d), respectively (presumably, present in solution as trifluoroacetates). These products, which are formally derived from the cations (12) and (13) by hydride shift from the methylene group of the cyclohexadienyl ligand to the C^+ centre, were identified by comparison of their [1]H n.m.r. spectra * with those of authentic cations in the same solvent. The rearranged cations were also isolated as their $[PF_6^-]$ salts which were found to be identical with the corresponding salts prepared earlier by ligand-exchange reactions.

Attempts to identify the (presumed †) first-formed cations (12) and (13) by recording the [1]H n.m.r. spectra of freshly prepared solutions of the alcohol precursors in cold CF_3CO_2H (−10 °C initially) were unsuccessful and it may be concluded that hydride-shift rearrangements occur extremely readily to give the more stable isomeric arenecyclopentadienyliron cations.

Mechanistic Study.—The mechanism of hydride migration could occur in principle either by an intra- or inter-molecular shift. For cations of the type (12), an intra-ionic process would require stereoselective interligand transfer of 6-*endo*-H of the methylene group of the cyclohexadienyl ring. In view of the known geometry of η^5-cyclohexadienylmetal complexes,‡ such a mechanism appears unlikely since flattening of the ligand to facilitate hydride transfer would be electronically disfavoured.[18] For cations of the type (13), however, intra-ionic migration of either 6-*exo*- or 6-*endo*-H is stereochemically feasible. Since hydride-exchange reactions of η^5-cyclohexadienylmetal complexes with

attached to a cationic arenecyclopentadienyliron residue,§ or a stereochemically and entropy disfavoured self-destructive process in which simultaneous exchange of two hydride groups between two cations occurs.

Dissolution of the 6-*exo*-deuterio-labelled alcohol (7b) in CF_3CO_2H led to rearrangement, as for the all-proton

TABLE 1

[1]H N.m.r. spectra of arenecyclopentadienyliron cations [a,b]

Compound	Arene protons (τ)	Cyclopentadienyl protons (τ)	Other protons (τ)
(3a)	3.69 (s)	4.90br (s)	7.50 (q, CH_2), 8.72 (t, Me) [c]
(3b)	3.87 (s)	5.00br (s)	6.32 (s, CH_2), 2.55—2.85 (m, Ph)
(4c)	3.86 (s)	5.04 (s)	7.52 (s, Me)
(4d)	3.79br (s)	4.98 (s)	7.0—7.5 (m, CH), 8.56 (d, Me) [c]
(9)	3.70 (s)	4.90br (s)	7.0—7.5 (m, CH), 8.75 (d, Me) [c,d]
(11)	3.72 (s)	4.92br (s)	8.75 (s, Me) [d]

[a] For $[PF_6^-]$ salts in CF_3CO_2H with Me_4Si as internal reference. [b] Integrated signal intensities agreed with assignments. [c] J ca. 7 Hz. [d] Lines broadened due to H–D coupling.

analogue (5d). Comparison of the [1]H n.m.r. spectrum of this freshly prepared solution with that of the unlabelled cumene complex (4d) in the same solvent showed that rearrangement had occurred predominantly but not exclusively by deuteride (rather than hydride) shift. Thus, superimposed and centred upon the characteristic methyl doublet resonance of the $CHMe_2$ group [*cf.* spectrum of (4d); Table 1] was a much more intense,

TABLE 2

[1]H N.m.r. spectra of neutral compounds [a,b]

Compound	Cyclopentadienyl protons (τ) [e]	Cyclohexadienyl protons (τ) [e]					Other protons (τ)
		1-, 5-H	2-, 4-H	3-H	6-*exo*-H [f]	6-*endo*-H	
(2a)	5.6—6.05	7.4—8.1	5.6—6.05	3.93 (tt)	8.60	7.4—8.1	5.38 (q, CH), 7.8 (OH), 8.53 (d, Me)
(2b)	5.65—6.15	7.5—8.15	5.65—6.15	4.00 (tt)	8.61	7.5—8.15	2.6—3.0 (Ph), 4.65 (s, CH), 7.30br (s, OH)
(5b)	5.74 (s)	6.9—7.6	4.70 (dt), 5.3—5.5	3.65 (td)	8.70	6.9—7.6	6.30 (s, OMe)
(5c)	5.83 (s)	7.7—8.1	5.6—5.95	4.05 (td)	8.75	7.7—8.1	6.16, 6.52 (2d, CH_2),[g] 7.8 (OH)
(5d)	5.73 (s)	7.4—8.1	5.5—5.8	3.94 (td)	8.72	7.4—8.1	7.7 (OH), 8.68, 8.88 (2s, Me_2)
(5e)	5.86 (s)	7.5—8.1	5.7—6.1	4.12 (tt)	8.65	7.5—8.1	8.63 (s, Me)
(7a)	5.75 (s)	6.9—7.6	4.72 (dt), 5.3—5.5	3.68 (td)		6.9—7.6	6.32 (s, OMe)
(7b)	5.73 (s)	7.4—8.1	5.5—5.8	3.92 (td)		7.4—8.1	7.9 (OH), 8.7, 8.9 (2s, Me_2)
(8)	6.08br(s)						7.4—7.95 (m, CH), 8.87 (d, Me) [c,d]
(10)	6.12br(s)						8.87 (s, Me) [d]

[a] For solutions in $CDCl_3$, with Me_4Si as internal reference. [b–d] As for Table 1. [e] m, unless indicated otherwise. [f] d, J ca. 12 Hz. [g] J ca. 16 Hz.

triphenylmethyl cation are known [15] to occur by stereospecific transfer of 6-*exo*-H, similar selectivity would be expected for inter-cationic hydride-transfer reactions of the cations (12) and (13). However, such reactions would require either the concomitant generation of an unlikely dicationic species, in which a C^+ substituent is

slightly broadened ¶ singlet attributable to the $CDMe_2$ group of the cation (4e). Independent experiments established that the $CHMe_2$ substituted product does not arise by H–D exchange of the $CDMe_2$ substituted complex with solvent (CF_3CO_2H). Assuming an intramolecular mechanism, this result suggests that cations

* Resonances due to unidentified minor products (< 10%) were always present in the spectra of these solutions. The identity of the major product was substantiated in each case by addition of an authentic sample to the solution and observation of the expected [1]H n.m.r. signal enhancements.

† It is conceivable that the conjugate acids ($R\overset{+}{O}H_2$) of the alcohols undergo concerted dehydration and hydride transfer.

‡ A survey of the known crystal structures of such complexes has been provided.[18]

§ Alternatively, hydride transfer from the cyclohexadienyl ligand could be accompanied by capture of solvent (CF_3CO_2H) by the C^+-centre of the donor cation.

¶ An H–D spin–spin coupling constant is much lower (ca. 15%) than the corresponding H–H constant (ca. 7 Hz for $CHMe_2$).

of the type (13) rearrange by preferential 1,3-shift of 6-*exo*-H of the methylene group.† The reported [13] formation of the tricarbonyl(1-methylcyclohexadienyl)-iron cation on acid treatment of tricarbonyl[1-(hydroxy-methyl)cyclohexa-1,3-diene]iron may occur by a similar mechanism involving the cation (14) as a potential or actual intermediate.

In solution in CF_3CO_2H, the alcohol (6) also rearranged as for its all-proton analogue (2a). Operation of an intramolecular hydride shift would have led stereo-selectively to the trifluoroacetate salt of the cation (9) containing a second deuterium label in the benzene ring. However, from the appearance of the methyl resonances in the [1]H n.m.r. spectrum of the product as an over-lapping singlet and doublet, each broadened by H–D coupling,¶ the reaction instead afforded a mixture of products containing a CHDMe and a CD_2Me substituent in the cyclopentadienyl ring [*cf.* spectra of (9) and (11); Table 1]; although mechanistically unlikely, the pre-sence of product containing an unlabelled ethyl group

(15)
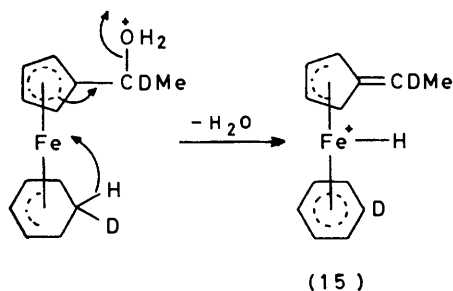
SCHEME 2

cannot be excluded. When the reaction was repeated using CF_3CO_2D as solvent, the proportion of the CD_2Me containing product was substantially increased. Al-though intermolecular processes must also be involved, this last observation suggests the possibility of a mechan-ism involving the intermediate (15), formed as indicated (Scheme 2). In $CF_3CO_2H(D)$, rearrangement to product by hydrogen shift or by concerted fulvene ligand proton-ation (deuteronation)–metal deprotonation can be envisaged, and H–D exchange with solvent of the metal-bonded hydrogen may also be considered.

We were unable to study related reactions in aprotic media. Thus, attempts to prepare esters (acetate, *p*-nitrobenzoate, *etc.*) of the alcohols (2a and b) and (5c and d), with a view to solvolysis studies, led to decom-position and a similar lack of success attended efforts to generate cations of the types (12) and (13) by hydroxide abstraction from the alcohols.

EXPERIMENTAL

All reactions were carried out under pure nitrogen. Chromatography was carried out using neutral alumina, prepared as described previously.[12] Light petroleum refers to the fraction of b.p. 40—60 °C. [1]H N.m.r. spectra (Tables 1 and 2) were recorded on a Perkin-Elmer R12A spectrometer at 60 MHz and i.r. spectra on a Perkin-Elmer 457 spectrometer. Molecular weights were determined by

accurate mass measurement of the molecular ions in the mass spectra, obtained using an A.E.I. MS9 spectrometer at 70 eV.

(η^5-*Cyclohexadienyl*)[(1-*hydroxyethyl*)-η^5-*cyclopentadienyl*]-*iron* (2a).—A mixture of the salts (1a) and (4a) (*ca.* 4 : 1 respective molar proportions) was prepared from acetyl-ferrocene by ligand exchange with benzene according to the published method.[11] Sodium borohydride (1.0 g) was added in portions to a solution of this mixture (2.0 g) in 1,2-dimethoxyethane (50 ml). The solution was stirred for 20 h, then diluted with water, and extracted thoroughly with ether. The ether extract was washed several times with water, dried ($MgSO_4$), and evaporated, and the residual oil was chromatographed. Light petroleum eluted the complex (5a) (0.18 g) which was identified by comparison with an authentic sample. Ether eluted the *alcohol* (2a) (0.55 g), a viscous orange liquid (Found: *M*, 244.055 2. $C_{13}H_{16}FeO$ requires *M*, 244.055 0); $\nu_{max.}$ (CCl_4) 3 400 cm^{-1} (OH). This alcohol is unstable in solution but can be stored for limited periods in the dark under nitrogen in a deep-freeze.

(6-exo-*Deuterio*-η^5-*cyclohexadienyl*)[(1-*deuterio*-1-*hydroxy-ethyl*)-η^5-*cyclopentadienyl*]*iron* (6).—This alcohol was pre-pared exactly as for (2a) except that $NaBD_4$ was used in place of $NaBH_4$. The product was an unstable orange liquid (Found: *M*, 246.068 2. $C_{13}H_{14}D_2FeO$ requires *M*, 246.067 4); $\nu_{max.}$ (CCl_4) 3 400 cm^{-1} (OH).

(η^5-*Cyclohexadienyl*)[(1-*hydroxybenzyl*)-η^5-*cyclopentadi-enyl*]*iron* (2b).—A mixture of the salts (1b) and (4a) (*ca.* 20 : 1 respective molar proportions) was prepared from benzoylferrocene by ligand exchange with benzene accord-ing to the published method.[11] A solution of this mixture (2.0 g) in 1,2-dimethoxyethane was reduced with $NaBH_4$ exactly as described in a previous experiment, and the product was chromatographed. Light petroleum eluted a trace of the complex (5a). Ether eluted the *alcohol* (2b) (0.67 g), a viscous orange liquid (Found: *M*, 306.071 0. $C_{18}H_{18}FeO$ requires *M*, 306.070 7); $\nu_{max.}$ (CCl_4) 3 410 cm^{-1} (OH).

(η^6-*Benzene*)(η^5-*ethylcyclopentadienyl*)*iron Hexafluorophos-phate* (3a).—A solution of 1,1′-diethylferrocene (4.8 g, 0.02 mol) in dry benzene (50 ml) was refluxed with stirring for 6 h with powdered aluminium chloride (5.5 g) and aluminium powder (0.5 g). The colour of the mixture changed from yellow through light green to red-brown. The mixture was cooled, water (100 ml) added carefully, and the mixture stirred vigorously for a few minutes. The yellow aqueous layer was separated, washed thoroughly with light petrol-eum, and a saturated aqueous solution of NH_4PF_6 was added. The title salt (1.9 g, 25%) was precipitated as a yellow solid which was purified by reprecipitation from acetone solution by addition of ether, m.p. 160° (decomp.) (lit.,[20] 162°).

(η^6-*Benzene*)(η^5-*benzylcyclopentadienyl*)*iron Hexafluoro-phosphate* (3b).—This salt was prepared from 1,1′-dibenzyl-ferrocene by ligand exchange with benzene using the method described in the previous experiment, and was obtained (15%) as a yellow solid, m.p. 158° (decomp.) (lit.,[20] 161—162°).

(η^6-*Toluene*)(η^5-*cyclopentadienyl*)*iron Hexafluorophos-phate* (4c).—This salt was prepared from ferrocene by ligand exchange with toluene as described earlier,[13] m.p. 163° (decomp.) (lit.,[20] 165°).

(η^6-*Cumene*)(η^5-*cyclopentadienyl*)*iron Hexafluorophosphate* (4d).—This salt was prepared from ferrocene by ligand

exchange with cumene, and was obtained as a yellow solid, m.p. 85° (decomp.) (lit.,[20] 83—85°).

(1-*Hydroxymethyl*-η^5-*cyclohexadienyl*)(η^5-*cyclopentadienyl*)-*iron* (5c).—Lithium aluminium hydride (50 mg) was added to a solution of the ester (5b)[12] (0.26 g, 1.0 mmol) in dry ether (50 ml) and the mixture was stirred at -10 °C for 1 h. The solution was then washed with ice–water, dried (MgSO$_4$), and evaporated under reduced pressure, maintaining the solution temperature below 0 °C. The *alcohol* (5c) (0.21 g, 91%) remained as an orange-red low melting solid (Found: M, 230.039 8. $C_{12}H_{14}FeO$ requires M, 230.039 4); $\nu_{max.}$ (CCl$_4$) 3 560 cm^{-1}. This product was unstable in solution and in the absence of solvent.

When this experiment was conducted at room temperature with a larger excess of reducing agent, the only product isolated was the complex (5e), an orange-red liquid identified by comparison with an authentic sample.[13]

[1-(1-*Hydroxy*-1-*methylethyl*)-η^5-*cyclohexadienyl*](η^5-*cyclopentadienyl*)*iron* (5d).—An excess of methyl-lithium (*ca.* 2M in ether) was added to a solution of the ester (5b)[12] (0.26 g, 1.0 mmol) in dry ether (50 ml) and the mixture was stirred for 2 h at room temperature. The solution was then washed with ice–water, dried (MgSO$_4$), and evaporated under reduced pressure at low temperature, leaving the *alcohol* (5d) (0.24 g, 90%) as a viscous orange-red liquid (Found: M, 258.071 6. $C_{14}H_{18}FeO$ requires M, 258.070 7); $\nu_{max.}$ (CCl$_4$) 3 550 cm^{-1} (OH). This product was unstable in solution and in the absence of solvent, and decomposed during column chromatography (neutral Al$_2$O$_3$) or t.l.c. (SiO$_2$).

[6-exo-*Deuterio*-1-(1-*hydroxy*-1-*methylethyl*)-η^5-*cyclohexadienyl*](η^5-*cyclopentadienyl*)*iron* (7b).—The 6-*exo*-deuterio-labelled ester (7a) was prepared by reduction of the salt (4b) with NaBD$_4$ exactly as described[12] previously for the corresponding NaBH$_4$ reduction. This ester was converted into the *alcohol* (7b) (92%) by reaction with methyl-lithium as described in the preceding experiment. The product was obtained as an unstable viscous liquid (Found: M, 259.077 6. $C_{14}H_{17}DFeO$ requires M, 259.076 8); $\nu_{max.}$ (CCl$_4$) 3 550 cm^{-1} (OH).

1,1′-*Bis*-(1-*deuterioethyl*)*ferrocene* (8).—A solution of 1,1′-bis-(1-hydroxyethyl)ferrocene[21] (0.55 g, 2.0 mmol) in dry ether (5 ml) was added to a stirred suspension of LiAlD$_4$ (0.32 g) and powdered Al$_2$Cl$_6$ (1.35 g) in ether (25 ml). The mixture was stirred overnight and then poured carefully into water. The ether layer was separated, washed with water, dried (MgSO$_4$), and evaporated, and the residue was dissolved in light petroleum and chromatographed on t.l.c. plates (SiO$_2$). The *ferrocene* (8) (0.44 g, 89%) was obtained as a mobile yellow liquid, identified by comparison of its ^{1}H n.m.r. spectrum with that of 1,1′-diethylferrocene.

1,1′-*Bis*-(1,1-*dideuterioethyl*)*ferrocene* (10).—The reduction of 1,1′-diacetylferrocene[22] with LiAlD$_4$–Al$_2$Cl$_6$ was carried out as described in the preceding experiment and the product was purified by t.l.c. The *ferrocene* (10) (85%) was obtained as a mobile yellow liquid, identified by comparison of its ^{1}H n.m.r. spectrum with that of 1,1′-diethylferrocene.

(η^6-*Benzene*)[(1-*deuterioethyl*)-η^5-*cyclopentadienyl*]*iron Hexafluorophosphate* (9).—This *salt* was prepared (40%) by ligand exchange of the ferrocene (8) with benzene, according to the method described earlier for the preparation of (3a), and identified by its ^{1}H n.m.r. spectrum.

(η^6-*Benzene*)[(1,1-*dideuterioethyl*)-η^5-*cyclopentadienyl*]*iron Hexafluorophosphate* (11).—This *salt* was prepared (45%) by ligand exchange of the ferrocene (10) with benzene, according to the method described earlier for the preparation of (3a), and identified by its ^{1}H n.m.r. spectrum.

Hydride-shift Reactions.—The following general procedures were used. Cold CF$_3$CO$_2$H (*ca.* -10 °C), which had been deoxygenated by passage of nitrogen, was added rapidly to a cold n.m.r. sample tube containing the alcohol and Me$_4$Si reference under nitrogen. The ^{1}H n.m.r. spectrum of the resulting solution (*ca.* 0.2M) was recorded immediately. Repeated scans showed no change in the spectra other than a slow deterioration in quality. Identification of the species present (see Discussion section) was achieved by addition to the solution of an authentic sample of the [PF$_6^-$] salt of the suspected cation and observation of enhancement of the appropriate signals. Identification was confirmed by isolation. A freshly prepared solution of the alcohol in CF$_3$CO$_2$H was diluted with water and filtered free of impurities, and an excess of a saturated aqueous solution of NH$_4$PF$_6$ was added. The precipitated [PF$_6^-$] salt was purified by reprecipitation from acetone solution by addition of ether, and identified by comparison (i.r. spectrum, *etc.*) with an authentic sample.

REFERENCES

[1] Part 17, T. S. Abram, W. Crawford, A. C. Knipe, and W. E. Watts, *Proc. Roy. Irish Acad.*, 1977, **77B**, 317.

[2] L. Haynes and R. Pettit in 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley–Interscience, New York, 1977, vol. 5.

[3] W. E. Watts, *J. Organometallic Chem. Library*, in the press.

[4] N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, 1970, **92**, 3065; D. E. Kuhn and C. P. Lillya, *ibid.*, 1972, **94**, 1682.

[5] R. E. Davis, H. D. Simpson, N. Grice, and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 6688; C. S. Eschbach, D. Seyferth, and P. C. Reeves, *J. Organometallic Chem.*, 1976, **104**, 363.

[6] D. Seyferth, personal communication.

[7] N. M. Loim, L. A. Malutschenko, Z. N. Parnes, and D. N. Kursanov, *J. Organometallic Chem.*, 1976, **108**, 363; A. G. Ginzburg, V. N. Setkina, P. V. Petrovskii, Sh. G. Kazumov, G. A. Panosyan, and D. N. Kursanov, *ibid.*, 1976, **121**, 381; *Doklady Akad. Nauk S.S.S.R.*, 1976, **228**, 1386.

[8] J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometallic Chem.*, 1965, **4**, 324; G. A. Olah and S. H. Yu, *J. Org. Chem.*, 1976, **41**, 1694; M. Acampora, A. Ceccon, M. Dal Farra, G. Giacometti, and G. Rigatti, *J.C.S. Perkin II*, 1977, 483.

[9] D. Seyferth, G. H. Williams, and D. D. Traficante, *J. Amer. Chem. Soc.*, 1974, **96**, 604; D. Seyferth, G. H. Williams, A. T. Wehman, and M. O. Nestle, *ibid.*, 1975, **97**, 2107.

[10] Preliminary communication, M. M. Khan and W. E. Watts, *J. Organometallic Chem.*, 1976, **108**, C11.

[11] D. Astruc and R. Dabard, *Tetrahedron*, 1976, **32**, 245.

[12] J. F. McGreer and W. E. Watts, *J. Organometallic Chem.*, 1976, **110**, 103.

[13] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (*C*), 1968, 2257.

[14] See R. G. Sutherland, *J. Organometallic Chem. Library*, 1977, **3**, 311.

[15] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (*C*), 1969, 2024.

[16] P. J. C. Walker and R. J. Mawby, *J.C.S. Dalton*, 1973, 622; *Inorg. Chim. Acta*, 1973, **7**, 621; A. Mawby, P. J. C. Walker, and R. J. Mawby, *J. Organometallic Chem.*, 1973, **55**, C39; P. L. Pauson and J. A. Segal, *J.C.S. Dalton*, 1975, 1683; G. A. M. Munro and P. L. Pauson, *Israel J. Chem.*, 1976—1977, **15**, 258; A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shilovtseva, and V. A Petrakova, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1975, 1151.

[17] D. S. Trifan and R. Bacskai, *J. Amer. Chem. Soc.*, 1960, **82**, 5010.

[18] R. Hoffmann and P. Hofmann, *J. Amer. Chem. Soc.*, 1976, **98**, 598.

[19] A. J. Birch and D. H. Williamson, *J.C.S. Perkin I*, 1973, 1892.

[20] D. Astruc and R. Dabard, *Bull. Soc. chim. France*, 1975, 2571.

[21] T. A. Mashburn and C. R. Hauser *J., Org. Chem.* 1961, **26**, 1671.

[22] M. Rosenblum and R. B. Woodward, *J. Amer. Chem. Soc.*, 1958, **80**, 5443.